Historical Profiles of Chlorinated Paraffins and Polychlorinated Biphenyls in a Dated Sediment Core from Lake Thun (Switzerland)

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A dated sediment core from Lake Thun covering the last 120 years was analyzed to get an overview of the historical trend of the chlorinated paraffin (CP) and polychlorinated biphenyl (PCB) deposition, because CPs and PCBs have/had similar applications as plasticizers and flame retardants. Total CP concentrations (sum of short chain (SCCP), medium chain (MCCP), and long chain CPs (LCCP)) showed a steep increase in the 1980s and a more-or-less stable level of 50 ng g^{-1} dry weight (dw) since then. The concentration-time profile is in good agreement with the available information on global production data. The quantification of higher chlorinated SCCPs using electron capture negative ionization low resolution mass spectrometry (ECNI-LRMS) revealed an increase in recent years. In addition, the degree of chlorination of SCCPs has strongly increased during the past 40 years, which may indicate its use as an additive for plastics, paints, and coatings. Furthermore, PCBs were analyzed in dated sediment slices. The PCB concentrations (sum of the six indicator congeners) peaked around 1969 (18 ng g^{-1} dw) and decreased to 1.3 ng g^{-1} dw in the surface layer corresponding to 2004. The peak level of CPs exceeded those of PCBs by about a factor of 3.

Introduction

Chlorinated paraffins (CPs), also known as polychlorinated *n*-alkanes (PCAs) or chloroparaffins, are industrial chemicals introduced in the 1930s (*1*). Their actual global annual production is estimated to approximately 300 000 tons (*1*). Based on the most recently available information on production data (*2*) a total amount of more than 7 000 000 tons of CPs has been produced since their introduction. They are mainly used as additives in metal working fluids, as flame retardants, and as plasticizers (*3*). CPs are subdivided into short chain (SCCPs, C$_{10-13}$), medium chain (MCCPs, C$_{14-17}$), and long chain compounds (LCCPs, C$_{>17}$) with chlorine contents between 30 and 70% (*1*). CPs with high chlorine content (>65%) are mainly used as flame retardants (*2*).

Because of their persistence, CPs are ubiquitous in the environment, and they have a high potential for bioaccumulation (log K_{OW} = 4.4–8, depending on the chlorination degree) (*1*). Whereas the acute toxicity of CPs is generally low, chronic toxicity in aquatic organisms has been observed for SCCPs (*2*). Furthermore, SCCPs are carcinogenic in rats and mice (*4*) and were categorized in group 2B as "possibly carcinogenic to humans" by the International Agency for Research on Cancer (IARC) (*2*). They have been included in the list of priority hazardous substances of the European Water Framework Directive (*5*). In addition, SCCPs are now under discussion to be included in the Stockholm Convention on persistent organic pollutants (POPs) (*6*).

Currently, information on environmental levels is scarce as compared to other POPs such as polychlorinated biphenyls (PCBs), dioxins, and organochlorine pesticides. The main reason is the demanding analysis of CPs in environmental matrices due to their complex composition. So far, worldwide, only a few data on CP levels in lakes (*7–10*) as well as in the Swiss environment are available (*11–13*). A review of current analytical methods employed in the past five years and their applicability to different matrices was presented by Zencak and Oehme (*14*).

PCBs were used for similar applications as CPs, such as additives in cutting oils, paints, coatings, sealings, and as plasticizers. Although the toxicity of PCBs is higher than of CPs (*2, 15*), the environmental behavior of both contaminants is similar. Industrial production of PCBs started in the 1930s and ceased in the 1970s. About 1 300 000 tons of PCBs were produced during this period (*16*). The use of PCBs was prohibited for open systems such as printing inks, sealants, and cutting oils in Switzerland in 1972 (*17*). In 2004, the Stockholm Convention on POPs issued a ban of PCBs in 128 countries (*6*).

The aim of this work was to get an overview of the temporal trends of CP and PCB concentrations in a dated sediment core from Lake Thun covering the past 120 years. Studies of dated sediment cores are an excellent way to investigate concentration trends over decades. Time-related profiles of CPs and PCBs were discussed and were compared with other studies. Moreover, evidence of a partial substitution of PCBs by CPs was evaluated. Furthermore, similarities and differences in the observed congener group patterns were studied.

Two analytical techniques were applied for the in-depth characterization of CPs. First, screening of CP levels in 15 sediment slices was performed using a recently developed technique (*18*) based on gas chromatography (GC) combined with electron ionization tandem mass spectrometry (EI-MS/MS). This method enables the determination of total SCCPs, MCCPs, and LCCPs (total CPs, totCPs). Electron capture negative ionization low resolution mass spectrometry (ECNI-LRMS) supplied additional information for the characterization of CPs regarding the degree of chlorination as well as the congener and the homologue patterns in all slices from the past 40 years (*19, 20*). This is a demanding task because gas chromatographic and mass spectrometric overlap of SCCPs and MCCPs can lead to corruption of quantitation results. To minimize such effects, possible interferences have to be identified and eliminated (*21*). Therefore, the method of Reth et al. was employed to allow a minimization of such interferences (*22*).

Materials and Methods

Sampling. A sediment core from Lake Thun was taken on May 18, 2005 near the mouth of the river Aare (46°39′53″ N, 7°48′54″ E, near the village Därligen) at a depth of 60 m using

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a gravity corer. Lake Thun is located in the alpine region of the Canton Bern in the center of Switzerland and has a surface area of 47.69 km^2, a mean depth of 136 m, and a volume of 6.42 km^3. Lake Thun is situated in a rural, densely populated catchment area without known point sources such as, for example, metal and polymer industries. The core was 1.1 m in length and 56 mm in diameter. It was cut into 1 cm slices that were lyophilized, weighed, homogenized, and stored in glass jars in the dark before dating and analysis.

Sediment Core Dating and Flux Calculations. Dating of the sediment core by ^{137}Cs and ^{210}Pb (*23*) analysis as a function of depth revealed an average sedimentation rate of 0.45 cm per year (see Supporting Information Figure S1). Thus, the 1 cm thick surface layer corresponds to the deposition of year 2004.

Fluxes (μg m^{-2} y^{-1}) were calculated for each sediment slice:

$$\text{Flux} = \frac{c_{\text{totCP}} \times r_{\text{sed}} \times \text{wt}_{\text{s}}}{v_{\text{s}}} \quad (1)$$

where c_{totCP} is the total CP concentration in each slice obtained by EI-MS/MS (μg g^{-1} dry weight), r_{sed} is the sedimentation rate in each slice (m y^{-1}), wt$_{\text{s}}$ is the total dry weight (dw) of the sediment slice (g) and v_{s} is the volume of the slice (m^3).

Chemicals. Cyclohexane, dichloromethane (DCM), *n*-hexane (*n*Hex) and toluene for residue analysis were obtained from Biosolve (Vallenswaard, Netherlands). Reference SCCP (chlorine contents of 51.5, 55.5, and 63.0%) and MCCP mixtures (chlorine contents of 52.0 and 57.0%) with concentrations of 100 ng μL^{-1} in cyclohexane as well as ϵ-hexachlorocyclohexane (ϵ-HCH, solution in cyclohexane, 10 ng μL^{-1}) were purchased from Ehrenstorfer GmbH (Augsburg, Germany). ^{13}C$_{10}$-*trans*-chlordane (100 ng μL^{-1}, solution in *n*-nonane, purity 99%) and ^{13}C$_{12}$-PCBs standard mixture containing the congeners 28, 52, 101, 138, 153, 180 were supplied by Cambridge Isotope Laboratories (Andover, USA). ^{15}N$_3$-musk xylene (1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, ^{15}N$_3$-MX) was synthesized in our laboratories (*24*). Copper powder (63 μm), silica gel for column chromatography (230–400 mesh, 0.045–0.063 mm), and sulfuric acid (98%) were obtained from Merck KGaA (Darmstadt, Germany). Florisil PR (60–100 mesh) and anhydrous sodium sulfate (Pestanal) were purchased from Fluka (Buchs, Switzerland). Florisil, sodium sulfate, and silica gel were dried overnight at 220 °C.

Extraction and Clean-up. Details of the applied cleanup procedure are given elsewhere (*25, 26*) and, hence, are only briefly described. A 5–10 g portion of dried and homogenized sediment was spiked with the corresponding internal standards (CP analysis: 10 ng of ^{13}C$_{10}$-*trans*-chlordane; PCB analysis: 8 ng of a ^{13}C$_{12}$-PCB-mixture) and then Soxhlet extracted with 200 mL of DCM and *n*Hex (DCM/*n*Hex, 1:1, v/v) for 8 h. Sulfur was eliminated by the addition of activated copper powder. After solvent evaporation, sample matrix not persistent to sulfuric acid was removed by column chromatography on 20 g of silica gel impregnated with concentrated sulfuric acid (44%). PCBs and CPs were eluted with 70 mL of DCM/*n*Hex (1:1, v/v). Further fractionation was carried out on a glass column packed with 16 g of Florisil (1.5% water content) that was eluted with 75 mL of *n*Hex and 5 mL of DCM (first fraction) followed by 60 mL of DCM (second fraction). The first fraction containing PCBs was concentrated to 0.5 mL, and the solvent was changed to toluene. The remaining solvent was concentrated to about 100 μL, which was transferred to a GC vial containing the recovery standard (9.84 ng of ^{15}N$_3$-MX). The second fraction containing all CPs was concentrated to 0.5 mL, and the solvent was changed to cyclohexane. Finally, the extract was reduced to 100 μL, and 10 ng of ϵ-HCH in 10 μL of cyclohexane were added as recovery standard.

Quality Assurance. Extreme care was taken to keep background and cross contamination at a minimum. All glassware was washed in a glassware washer and immersed in a detergent bath (5% RBS35 concentrate, Fluka) for 12 h. Then, glassware and glass fiber thimbles (30 × 100 mm, 603G, Wathman, Schleicher & Schuell, Meidsone, England) were rinsed with DCM and *n*Hex and heated to 450 °C overnight. Prior to use, glassware was rinsed with the same solvents.

Method blanks were analyzed using the above-mentioned extraction and cleanup procedure. Blank concentrations calculated assuming a mean sample weight of 8.5 g dw were 3.3 ng g^{-1} dw and 0.1 ng g^{-1} dw for totCPs and ΣPCBs, respectively.

A "prechlorine industry" sediment slice (1899) was analyzed to detect possible cross-contamination during sampling. Whereas CP concentrations were similar to method blank levels (approximately 200% of method blank) concentrations of PCBs were slightly higher than the respective method blank levels (approximately 400% of method blank). In addition, the same sample was spiked with 30 ng of reference SCCPs (55% chlorine content) and 8 ng of a PCB mixture (congener 28, 52, 101, 138, 153, 180). The recoveries were 82 and 102%, respectively.

Reproducibility of the analytical method was tested by separate processing of the two halves of the same sediment slice (1993). The difference of these two samples was 14% for totCPs, 3% for the sum SCCPs, 8% for the sum of MCCPs, and 11, 2.8, 7.5, 23, 58, and 39% for the PCB congeners 28, 52, 101, 138, 153, and 180, respectively. The calculated chlorine contents of the two halves were 67.8 and 68.2% for SCCPs and 55.9 and 56.2% for MCCPs.

Instrumental Analysis of CPs. Instrumental analysis was performed on a gas chromatograph CP-3800 coupled to a 1200L triple quadrupole mass spectrometer (Varian, Walnut Creek, USA) using EI-MS/MS and ECNI-LRMS. The gas chromatograph was equipped with a split/splitless injector and a fused silica capillary column (15 m × 0.25 mm) coated with 0.25 μm of cross-linked methylphenylpolysiloxane (DB5-MS, J&W Scientific, Folsom, USA). The injector temperature was set to 275 °C. The transfer line temperature was 280 °C, and the ion source temperature was 200 °C. Splitless injections (3.0 min) of 2.5 μL volume were carried out with a Combi Pal autosampler (CTC Analytics, Zwingen, Switzerland).

GC-EI-MS/MS. Instrumental parameters are published elsewhere in detail and, hence, are only briefly described (*18*). The temperature program for the GC-EI-MS/MS analysis was as follows: 3 min isothermal at 100 °C, increased at 50 °C min^{-1} to 300 °C, then isothermal for 3 min. Helium (99.996%, Sauerstoffwerk Lenzburg, Lenzburg, Switzerland) was employed as carrier gas at a constant flow of 2 mL min^{-1}. The EI mass spectra were acquired at 70 eV electron energy with a filament emission current of 150 μA and a scan time of 0.25 s scan^{-1}. Collision-induced dissociation (CID) gas pressure (argon, 99.5%, Sauerstoffwerk Lenzburg) was set to 0.13 Pa. The mass spectrometer was regularly tuned to optimal performance using perfluorotributylamine for both quadrupoles at *m/z* 69, 219, and 502. The fragmentation masses were slightly modified for the determination of the total CP amount: *m/z* 91 → *m/z* 53 (collision energy: -10 eV), *m/z* 102 → *m/z* 67 (-10 eV), and *m/z* 104 → *m/z* 67 (-10 eV). The precursor ion *m/z* 383 [M − Cl]$^+$ and the product ion *m/z* 276 [M − 4Cl]$^+$ were selected for the detection of the internal standard ^{13}C$_{10}$-*trans*-chlordane (-28 eV).

GC-ECNI-LRMS. Parameters for the determination of homologue profiles and degrees of chlorination by ECNI-LRMS are described elsewhere (*19, 20*). The temperature program for the GC-ECNI-LRMS analysis was as follows: isothermal at 100 °C for 2 min, increase at 15 °C min^{-1} to 280 °C and isothermal for 4 min, then increase at 50 °C min^{-1}
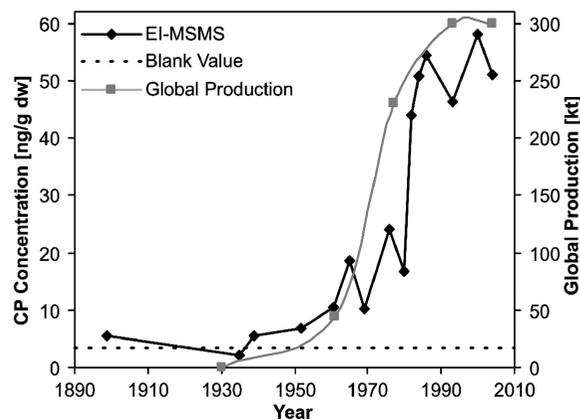
FIGURE 1. Historical time trend of total CP concentration (black line) in a sediment core from Lake Thun. Blank levels (dotted line) and global CP production (grey line) are also given. Analysis was performed by GC-EI-MS/MS.

to 300 °C and isothermal for 1.6 min. The mass spectrometer was employed in the ECNI mode with methane (99.995%, Carbagas, Rümlang, Switzerland) as reagent gas at an ion source pressure of 730 Pa. The transfer line temperature was set to 280 °C, and the ion source temperature was set to 200 °C. The ion source was tuned to optimum performance using perfluorotributylamine at m/z 283, 452, and 633. The most abundant isotopes of the $[M - Cl]^-$ ions of CPs with 5–13 chlorine atoms and of the $[M]^-$ ion (m/z 419.8) of $^{13}C_{10}$-trans-chlordane were recorded in the selected ion monitoring (SIM) mode (0.250 s dwell time per cycle). The most abundant isotope of the $[M - Cl]^-$ ion (m/z 254.9) was selected for the recovery standard ϵ-HCH.

ECNI-LRMS Identification and Quantification. Identification of the CP congener groups was performed by comparison of retention time, signal shape, and correct isotope ratio according to Reth and Oehme (21). The applied quantification procedure was described by Reth et al. (22). Using this method, a reliable quantification can be achieved even if the degree of chlorination of the samples and of the reference standards are different. For this purpose, three SCCP (51, 55, and 63% Cl) and two MCCP references (52 and 57% Cl) from Ehrenstorfer were used as described in ref 21.

PCB Analysis by GC-EI-HRMS. PCBs were determined using GC EI high resolution (HR) MS according to Schmid et al. (27).

Results and Discussion

Screening of Total CP Levels by GC-EI-MS/MS. The historical time trend of totCP concentrations in Lake Thun between 1899 and 2004 is shown in Figure 1. Each data point represents the average age of the respective sediment sample. Levels start at 5 ng g^{-1} dw for the deeper, preindustrial sediment slice, which is in the range of the blank concentrations, and rise slowly from the 1950s to the 1970s. Then, the totCP level increased more rapidly in the 1980s and became more or less stable in the 1990s to present. The maximum concentration of 58 ng g^{-1} dw was observed in 2000. The totCP concentration in the surface slice (2004) was slightly lower than the maximum level (51 ng g^{-1} dw). This trend is consistent with the few data available on global production (2), also shown in Figure 1.

Because totCP data determined by EI-MS/MS from other lake sediments are missing, the obtained data were compared with levels in other environmental matrices. Reth reported between 19 and 42 ng g^{-1} wet weight (ww) of totCPs in six brown trout samples from the Swiss rivers Liechtensteiner Binnenkanal and Necker and 25 ng g^{-1} ww in one lake trout sample from the Swiss alpine lake Lei da Diavolezza (12);
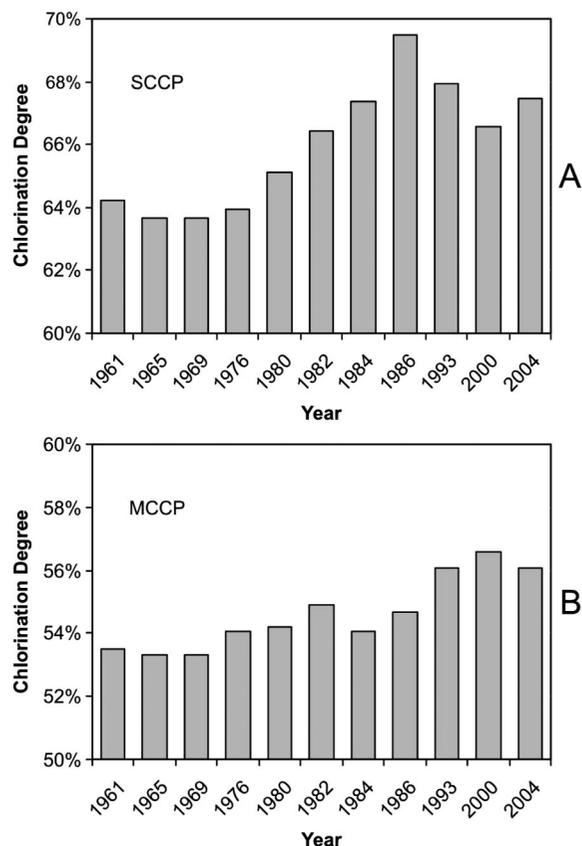
FIGURE 2. Degree of chlorination of the SCCP (A) and MCCP (B) congeners in a dated sediment core from Lake Thun obtained by GC-ECNI-LRMS.

totCP concentrations were between 5 and 499 ng g^{-1} dw in sediments from the North and Baltic Sea sampled from 2001 to 2003 (26).

CP Characterization by GC-ECNI-LRMS. Sediment samples after 1961 were analyzed by GC-ECNI-LRMS to determine "ECNI chlorine content" and chain length. The total ECNI chlorine contents of these sediment slices are shown in Figure 2. The degrees of ECNI chlorination of SCCPs were between 63.7 and 69.5% (surface: 67.5%). A very rapid increase could be observed during the 1980s. Obviously, these ECNI chlorine contents were rather high as compared to the chlorine contents of technical SCCP mixtures, being in the range 49–71%. Typically, CPs with high chlorine content are used as additives in plastics, paints, and coatings and not in metal working fluids. From these open system applications CPs can easily be released into the environment, including water systems. This change in chlorine content could be indicative for a change in the application of CPs.

The degree of ECNI chlorination of MCCPs was between 53.3 and 56.6% (surface: 56.1%).

A continuous increase of the ECNI chlorine content of SCCPs and MCCPs could be observed for the past 20 years. It is not possible to decide whether this shift is a consequence of increased usage of technical CP mixtures with higher chlorine content in recent years or if there is a significant dechlorination/biotransformation of CPs in older sediments.

SCCP and MCCP Concentrations. SCCPs and MCCPs were detected in all analyzed sediment slices (Figure 3). Comparison of the time profiles of totCPs, SCCPs, and MCCPs revealed that the rapid increase of totCP concentrations in the 1980s is mainly caused by SCCPs, whereas MCCP levels changed much less. The maximum SCCP concentration was 33 ng g^{-1} dw in 1986 (Figure 3), and the level of the surface sediment was 21 ng g^{-1} dw of SCCPs. MCCP concentrations increased since 1965 and reached a maximum in the surface
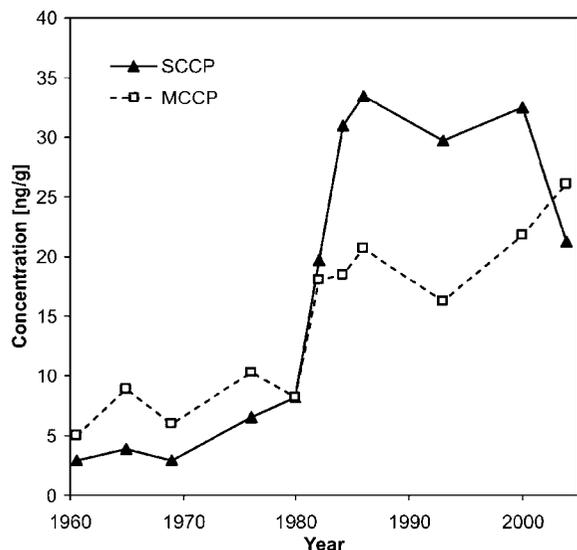
FIGURE 3. Historical time trends of SCCP (solid line) and MCCP (dashed line) concentrations obtained by GC-ECNI-LRMS.

sediment (26 ng g^{-1} dw) (Figure 3). SCCP and MCCP concentrations are compared in Figure 4A. The SCCP/MCCP ratio increased continuously from 1965 to 1993. A decrease of SCCPs and a shift to more MCCPs in the SCCP/MCCP ratio were observed after 2000 in the surface slice. Future research is planned to verify this decrease, which could be attributed to an effect of the regulations of the EU Water Framework Directive and the preceding discussions about a general ban of SCCPs.

The few data available for SCCP levels in surface lake sediments are from Canada (7, 8). The SCCP concentration in the Lake Thun surface sediment was considerably lower than in Lake Ontario (lake-wide average 49 ng SCCPs g^{-1} dw) (7), the southern basin of Lake Winnipeg (176 ng SCCPs g^{-1} dw) and Fox Lake (257 ng SCCPs g^{-1} dw) (8). Only concentrations of Lake Nipigon are similar to Lake Thun (18 ng SCCPs g^{-1} dw) (8). Three Canadian lakes had lower sediment concentrations (Ya Ya Lake 1.6 ng SCCPs g^{-1} dw, Hazen Lake 4.5 ng SCCPs g^{-1} dw, and the northern basin of Lake Winnipeg 8.0 ng SCCPs g^{-1} dw) (8).

For MCCPs in lake sediments there are even less studies available. Tomy and Stern reported a MCCP concentration in a surface lake sediment (Lake Erie, Canada, 68 ng MCCPs g^{-1} dw) (10), which was about three times higher than the maximum MCCP level in the surface sediment from Lake Thun. In 1985, Schmid and Müller found 5 ng MCCPs g^{-1} ww in surface sediment from Lake Zürich (11). The ww level in the respective sediment layer of Lake Thun is about four times higher, but these data cannot be directly compared because of a different analytical quantification method and not well-documented sampling.

Studies on river sediments revealed higher CP concentrations than surface sediment from Lake Thun, mainly due to the industrial catchment areas of these rivers (various rivers in the Czech Republic <2–347 ng g^{-1} dw SCCPs and <2–5575 ng g^{-1} dw MCCPs (28); river Besos, Spain 0.25–3.04 μg g^{-1} dw SCCPs (29); various rivers in Germany, France, and Norway 21–75 ng g^{-1} dw SCCPs and 24–153 ng g^{-1} dw MCCPs (30)).

So far, the only available data on historical profiles in sediments are findings on SCCPs in sediments from Canadian lakes. One profile from Lake Ontario (station 1007) exibited a maximum in 1970 with a concentration of about 800 ng g^{-1} dw SCCPs, which decreased to 410 ng g^{-1} dw SCCPs in the surface layer of 1996 (7). The other one (station 1034) has its maximum in the surface sediment (19 ng g^{-1} dw SCCPs in 1998) (7). In an investigation of six sediment cores from Canadian lakes, Tomy et al. reported concentration maxima
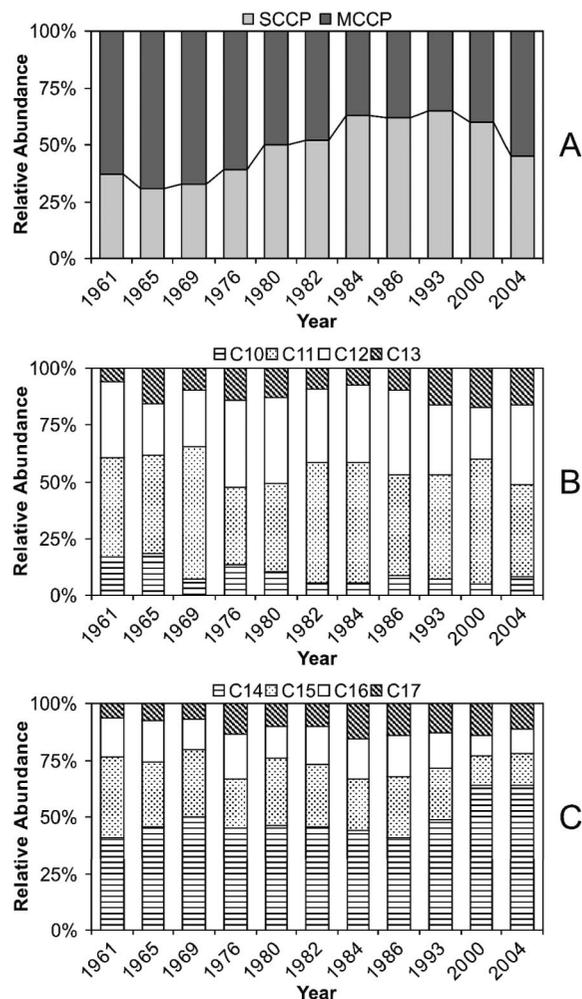
FIGURE 4. Chain length composition (A) as well as SCCP (B) and MCCP (C) homologue patterns of the sediment core from Lake Thun obtained by GC-ECNI-LRMS.

between the 1980s and the 1990s that were in the same range as in the sediment core from Lake Thun, but no clear temporal trend could be observed (8).

Homologue Patterns of CPs. In all sediment layers, C_{11} and C_{12} were the most abundant homologue groups within SCCPs (range: 66–87%; average: 79%; surface layer: 76%; see Figure 4B), which corresponds to technical SCCP mixtures (31). Within MCCPs, the C_{14} homologue group was most abundant (range: 41–64%; average: 48%; surface: 64%; see Figure 4C), which is also typical for technical mixtures.

Congener Patterns of CPs. Since the 1960s, a significant shift from lower to higher chlorinated congeners is observed in the pattern (see Figure 5 and Supporting Information Figures S2−4). Figure 5 shows the SCCP congener group pattern of sediment from 1961 (A) and of surface sediment from 2004 (B). SCCPs ($C_{10–13}$ chains) with eight chlorine atoms were predominant in 1961, whereas SCCPs with 9−10 chlorine atoms prevailed in surface sediment.

Comparison with PCB. Figure 6A shows the historical time profiles of CPs and PCBs (sum of the six indicator PCBs No. 28, 52, 101, 138, 153, and 180) in the sediment core from Lake Thun. PCBs emerged after 1940, and levels culminated around 1968, reaching a maximum concentration of 18 ng g^{-1} dw. Thereupon, the concentrations decreased continuously to 1.3 ng g^{-1} dw in the most recent surface layer from 2004. The swift decline after 1968 reflects the restrictions of PCB use. In Switzerland, the usage of PCBs in open systems was banned in 1972. At the same time, CP production started
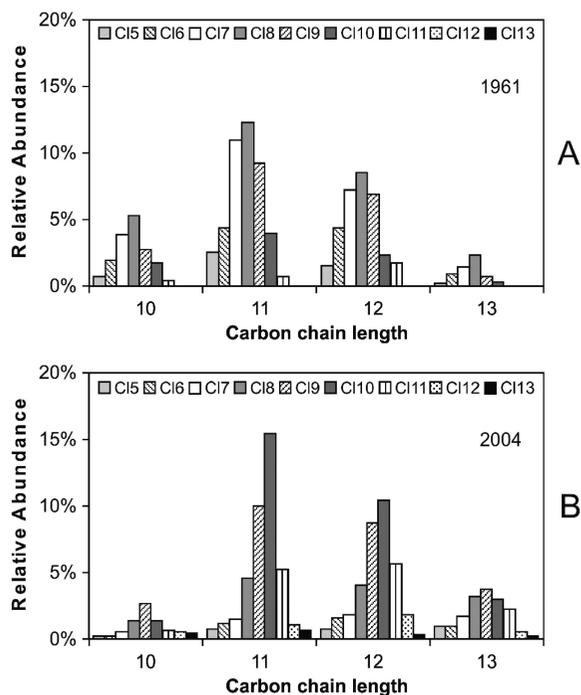
FIGURE 5. SCCP congener group patterns of the 1961 (A) and surface sediment slice (B) from Lake Thun determined by GC-ECNI-LRMS.
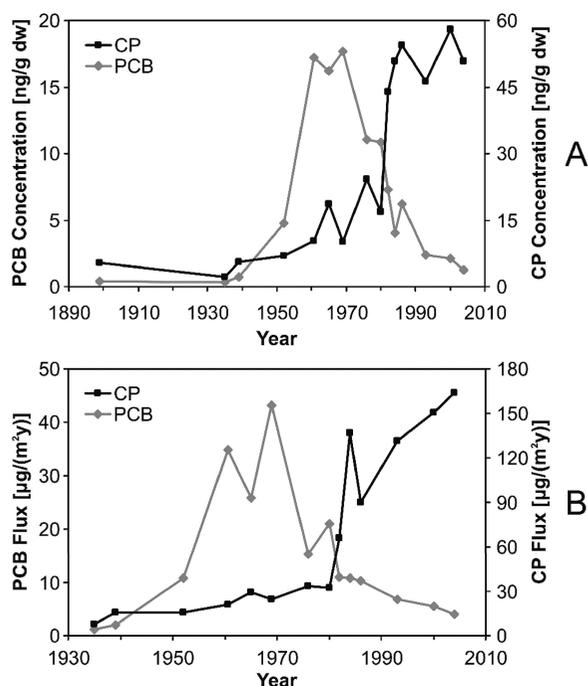
FIGURE 6. (A) Historical time trend of the sum concentration of CPs and PCBs in a sediment core from Lake Thun. Analysis was performed by GC-EI-HRMS and GC-EI-MS/MS, respectively. (B) Flux profiles of sum PCB (grey continuous line) and total CP (black continuous line) from 1937 to 2002.

to rise, partially as a consequence of its use as a substitute for PCBs and mainly due to the increased application of CPs as metal working fluids, plasticizers, and flame retardants. This change is reflected in the temporal trend of the CP levels shown in Figure 6A, as well. Furthermore, the peak concentration of 58 ng g^{-1} dw CPs is about 3 times higher than for PCBs (18 ng g^{-1} dw), which correlates well with the higher global production of CPs. A similar concentration profile of PCBs in a sediment core from the lake Greifensee located

near Zürich was reported by Zennegg et al. (*32*); however, the maximum concentration (130 ng g^{-1} dw, sum of the six indicator PCBs) was about 7 times higher, which is well compatible with more the urban and industrialized catchment area of this lake.

Fluxes and Inventory of CPs and PCBs. Annual CP and PCB (sum of the six indicator congeners) fluxes based on the respective concentrations measured in the sediment core from Lake Thun (see Figure 6B) were calculated using eq 1. The deposition flux of PCBs reached its maximum around 1969 (43 μg m^{-2} y^{-1}). This corresponds to a total annual PCB input of 2 kg y^{-1} into the sediment of the whole lake. Maximum deposition of CPs was observed in the most recent sediment layer, with 164 μg m^{-2} y^{-1}, corresponding to 8 kg y^{-1} for the whole lake. Total inventories estimated on the basis of these fluxes were 49 kg for PCBs and 185 kg for CPs. These data are in line with relative production amounts of the two chemicals for the whole period between 1935 and 2004 as given in the Introduction.

The calculated flux from the surface layer (164 μg m^{-2} y^{-1}) was higher for Lake Thun than for the Canadian lakes (0.45–147 μg m^{-2} y^{-1}) (*7, 8*). Only one lake (Lake Ontario, 170 μg m^{-2} y^{-1}) was comparable (*7*). Moreover, the SCCP flux was estimated for a sediment core from a lake in the Canadian Arctic (Devon Island). It showed a similar increase during the past 20 years (*9*). However, a maximum as observed for 1957 could not be detected for Lake Thun.

In conclusion, the sediment core from Lake Thun revealed a considerable deposition of CPs during the past 30 years. Comparison of the temporal trends of PCB and CP levels showed an increase of CPs when PCB levels declined. This is in line with a partial replacement of PCBs by CPs. The calculated fluxes and the high chlorine content provided an indication of a possible contamination by weak local sources releasing technical CP mixtures. However, further studies analyzing sediments from a defined spatial distribution and from the feeding rivers are necessary to obtain more information about local sources and possible transformation pathways.

Supporting Information Available

^{137}Cs and unsupported ^{210}Pb activity as a function of depth for the dating of the sediment core is shown in Figure S1. Figures S2−S4 show SCCP and MCCP congener group patterns of the sediment slices from Lake Thun between 1961 and 2004. This information is available free of charge via the Internet at http://pubs.acs.org.

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